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On the spectra of YCl molecule

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Abstract : The emission spectrum of YCl molecule has been re-investigated in the spectral region $\lambda\lambda$ 3545-4825 Å and $\lambda\lambda$ 5950-6700 Å using high temperature vacuum graphite furnace. The spectrum has been photographed at a reciprocal liner dispersion of 3 5 Å/mm at about a temperature of 2200°C in an atmosphere of argon. The study reveals the presence of a single system of bands in ultraviolet region but two system of bands in the blue violet region. The Janney's system ($\lambda\lambda$ 6300-6930 Å) was also found to extend in lower region upto λ 5950 Å. The analysis was confirmed by the presence of isotope effect for $Y^{35}Cl$ and $Y^{37}Cl$ in the bands of C—X, D—X and F—X systems.

Keywords : Thermal emission spectra, YCl molecule, vibrational isotope effect, vibrational analysis.

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1. Introduction

Janney [1] was the first to study the emission spectrum of YCl molecule in the region $\lambda\lambda$ 6300-6930 Å. He recorded 16 bands and classified them into a single system. On the basis of LIF study Fischell *et al* [2] reported two systems of bands lying in the spectral region $\lambda\lambda$ 4200-4600 Å and $\lambda\lambda$ 3600-3900 Å and determined approximate values of vibrational constants. Gopal *et al* [3] recorded the thermal emission spectrum of YCl molecule in the region $\lambda\lambda$ 4645-4065 Å and $\lambda\lambda$ 3855-3625 Å and classified the observed bands into four systems viz. D,E,F and G. In addition, Xin *et al* [4] photographed the thermal emission spectrum of YCl molecule in the region $\lambda\lambda$ 7700-9100 Å and reported the molecular constants. Recently on producing YCl molecule in a free jet molecular beam apparatus by chemical reaction in a laser produced plasma, Simard *et al* [5] reinvestigated the (o, o) bands of Janney's system and improved the rotational constants.

The analyses of the Fischell *et al* [2] and Gopal *et al* [3], are contrary to each other. Fischell *et al* [2] have classified the $\lambda\lambda$ 3600-3900 Å and $\lambda\lambda$ 4200-4600 Å bands each as a single system while Gopal *et al* [3] classified the $\lambda\lambda$ 3625-3855 Å and $\lambda\lambda$ 4065-4645 Å bands each to two systems viz. F, G and D, E respectively. The reported vibrational constants also differ in both the cases. Further the spectra recorded by Fischell *et al* [2] are at a very low resolution (1 Å) while the spectrum recorded by Gopal *et al* [3] is at a low

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dispersion (12-40 Å/mm). Therefore, the authors decided to re-examine the spectrum of YCl at a higher resolution (0.05 Å) and high dispersion (3.5 Å/mm) using high temperature graphite furnace.

The present paper reports our findings about YCl molecule.

2. Experimental

A small quantity of anhydrous yttrium chloride (Johnson Matthey) was put into the experimental tube of graphite furnace described by Saha *et al* [6]. After making necessary routine adjustments and evacuation of the furnace chamber, argon gas was introduced at a pressure of about 50 cm of mercury to minimise the rapid effusion of the molecular vapours from the open ends of the graphite tube. The substance was then vapourised to a temperature at about 2200°C to record good spectrogram in an exposure time of about 8 and 15 minutes in the spectral region $\lambda\lambda$ 5950-6700 Å and $\lambda\lambda$ 4200-4825 Å respectively. The spectrum has been recorded at a reciprocal linear dispersion of 3.5 Å/mm on ORWO 400 ASA black and white film using PGS-2 with a grating blazed at λ 5600 Å and total number of lines ruled 45600. The iron d.c. are spectrum was taken as comparison standard. The measurements were performed using Abbe comparator with least count of .0001 cm.

3. Results and discussion

Thermal emission spectrum of YCl molecule has been recorded in the region $\lambda\lambda$ 5950-6700 Å and $\lambda\lambda$ 3545-4825 Å and reproduced in Figures 1, 2 and 3. A total of 184 band heads, all are degraded to red, have been photographed out of which 50 are quite new ones. These bands have been classified into four systems : C—X, D—X, E—X and F—X. The following are the vibrational analyses proposed by the authors :

3.1. System C—X :

This system was studied for the first time by Janney [1] and was found to lie in the region $\lambda\lambda$ 6300-6930 Å. We have recorded the thermal emission spectrum of Janney's system for the first time and found that system extended in lower region up to λ 5950 Å. The recorded bands have been analysed into the $\Delta v = 6, 5, 4, 3, 2$ and 1 sequences in which the sequences $\Delta v = 4, 5$ and 6 are photographed for the first time. However we were unable to record (o, o) band (λ 6718.7 Å) because of the low sensitivity of the recording film. The extension in lower region is explained with the same vibrational constants as proposed by Janney [1]. The analyses is supported by the observed isotopic shifts in 26 bands.

The band head data, visual estimates of intensities and their vibrational assignments are collected in Table 1 while Table 2 lists the observed and calculated isotopic shifts between $Y^{35}Cl$ and $Y^{37}Cl$ bands.

3.2. System D—X and E—X :

These systems lie in the spectral region $\lambda\lambda$ 4000-4825 Å. Fischell *et al* [2] have recorded about 45 bands in the region $\lambda\lambda$ 4200-4600 Å and analysed all of them into single system.

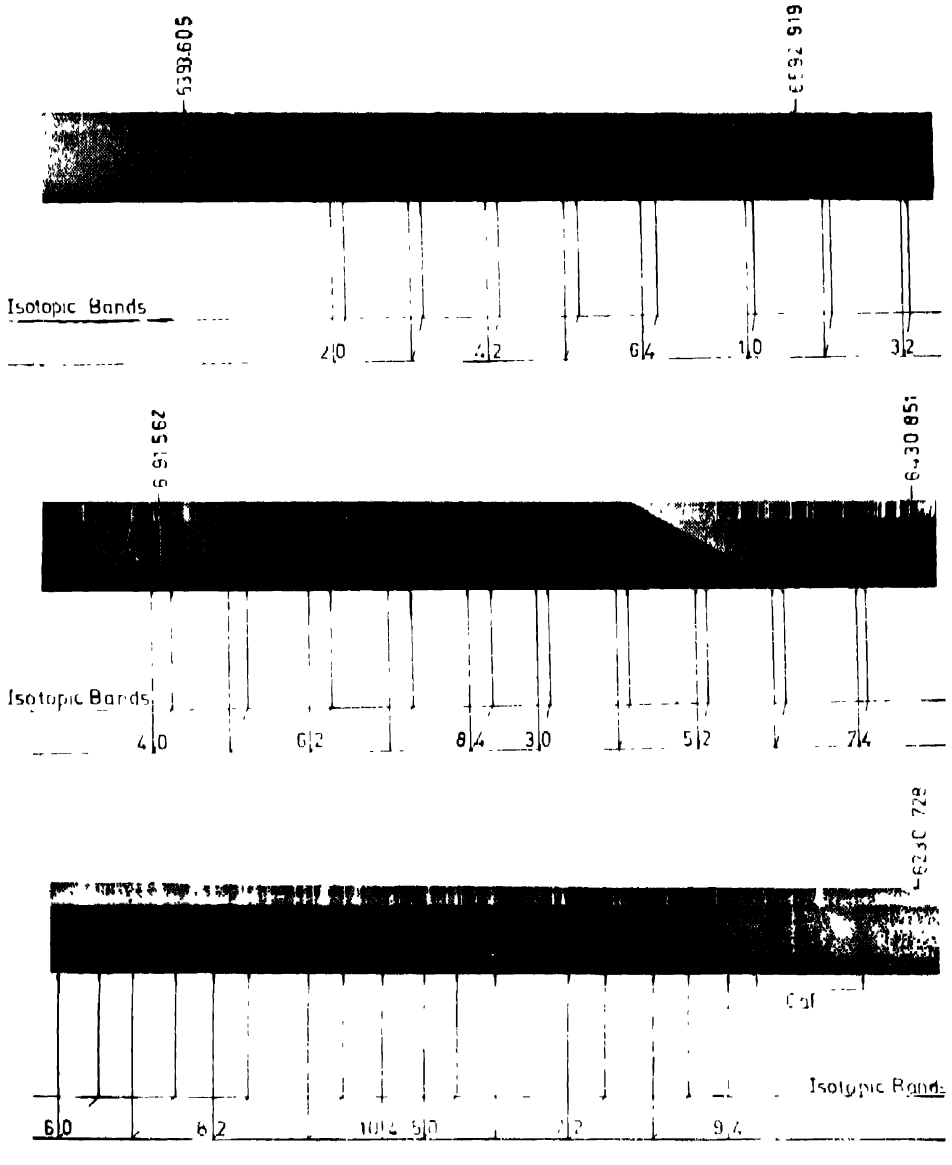

Figure 1. Thermal emission spectrum of YCl molecule.

We have been able to record about 167 bands and classified them into the two systems viz. D—X and E—X. The system D—X is well developed and consists of 117 bands while E—X system is relatively weak and consists of 50 bands. In the case of D—X system three new weak sequences viz. $\Delta v = -3, -4$ and -5 consisting of 29 bands have been identified. Further the analysis of the D—X system is confirmed by observing the isotope effect due to chlorine in case of 24 bands. The observed and calculated isotopic shifts agree well and collected in Table 2. Our analyses for these systems agree well with the one proposed by Gopal *et al* [3]. Table 1 contains band head data together with visual estimates of intensities and their classifications.

Table 1. Band head data of YCl molecule.

υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int.	υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')		Int.
	C—X System					D—X System			
15201.7	15201.5	1	0*	9	21513.5	21512.7	5	8	1
15143.6	15143.5	2	1*	8	21487.2	21486.3	6	9	1
15085.7	15085.2	3	2*	4	21461.0	21460.1	7	10	1
15521.7	15522.2	2	0*	9	21434.9	21432.9	8	11	1
15461.2	15461.5	3	1*	9	21408.9	21408.2	9	12	1
15401.1	15401.2	4	2*	8	21383.0	21382.2	10	13	1
15341.3	15341.0	5	3*	4	21357.2	21356.4	11	14	1
15281.8	15281.0	6	4	2	21331.5	21330.4	12	15	1
15839.3	15840.6	3	0*	4	21276.2	21275.9	0	4	1
15776.6	15777.2	4	1*	5	21252.0	21251.9	1	5	1
15714.2	15714.7	5	2*	7	21227.9	21226.4	2	6	1
15652.1	15652.1	6	3*	4	21203.9	21203.1	3	7	1
15590.4	15589.2	7	4*	4	21180.0	21178.9	4	8	1
16154.7	16153.6	4	0	3	21156.2	21157.2	5	9	1
16089.7	16090.7	5	1	6	21132.5	21132.7	6	10	1
16025.0	16025.9	6	2	5	21108.9	21107.8	7	11	1
15960.7	15960.9	7	3	4	21085.4	21086.7	8	12	1
15896.6	15897.1	8	4	3	21062.0	21061.8	9	13	1
16467.8	16469.1	5	0	2	21038.7	21039.3	10	14	1
16400.5	16402.6	6	1	1	21015.5	21015.7	11	15	1
16333.6	16332.7	7	2	1	20908.5	20908.2	0	5	1
16266.9	16267.1	8	3	1	20886.9	20885.3	1	6	1
16200.6	16201.1	9	4	1	20865.4	20866.2	2	7	1
16778.6	26778.7	6	0	1	20844.0	20846.0	3	8	1
16709.1	16707.5	7	1	1	20822.7	20821.3	4	9	1
16639.8	16638.6	8	2	1	20801.5	20800.1	5	10	1
16570.9	16572.8	9	3	1	20780.4	20779.2	6	11	1
16502.3	16500.4	10	4	1	20759.4	20758.3	7	12	1
					20738.5	20737.6	8	13	1

* Bands reported by Janney [1].

Table 1. (*contd.*)

υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')	Int.	υ_{cal} (cm^{-1})	υ_{obs} (cm^{-1})	(v', v'')	Int.
		F—X System					
26349.2	26348.1	0 2	4	26757.2	26755.6	8 8	1
26307.0	26306.8	1 3	3	27433.5	27433.5	1 0	6
26266.0	26266.7	2 4	3	27384.7	27385.0	2 1	5
26226.2	26225.1	3 5	2	27337.1	27336.7	3 2	4
26187.6	26186.3	4 6	2	27290.7	27291.6	4 3	2
26150.2	26149.4	5 7	1	27245.5	27246.3	5 4	1
26724.7	26724.7	0 1	7	27762.8	27762.9	2 0	3
26679.9	26680.3	1 2	5	27712.6	27712.3	3 1	4
26636.3	26637.2	2 3	5	27663.6	27763.8	4 2	2
26593.9	26595.1	3 4	3	27615.8	27614.7	5 3	2
26552.7	26551.8	4 5	2	27569.2	27568.7	6 4	1
26512.7	26510.9	5 6	1	27523.8	27524.2	7 5	1
27102.8	27102.8	0 0	10	27479.6	27480.2	8 6	1
27055.4	27056.2	1 1	8	28090.7	28091.3	3 0	1
27009.2	27010.3	2 2	4	28039 1	28037.9	4 1	2
26964.2	26964.0	3 3	2	27988.7	27989.9	5 2	2
26920.4	26918.8	4 4		27939.5	27938.1	6 3	2
26877.8	26876.6	5 5	1	27981.5	27890.8	7 4	1
26836.4	26835.1	6 6	1	27944.7	27843.5	8 5	1
26796.2	26797.3	7 7	1				

3.3. System F—X :

This system is recorded for the first time in thermal emission in the region $\lambda\lambda$ 3645-3850 Å. About 36 bands, all are degraded to red have been attributed to this system. The following vibrational constants are determined from the vibrational analyses :

$$\upsilon_{oo} = 27102.8 \quad \omega'_e = 332.1 \quad \omega'_e x'_e = 0.70 \quad \omega''_e = 380.7 \quad \omega''_e x''_e = 1.30 \text{ cm}^{-1}$$

The analysis is confirmed by observing the vibrational isotope shifts due to chlorine in 12 bands and presented in Table 2.

The values of the ground state vibrational constants in the present systems are assumed to be identical to those obtained by Janney [1] and it was unnecessary to alter these vibrational constants to explain all the observed bands in a satisfactory manner. The maximum difference between the observed and calculated bands are 2.1 cm^{-1} for the bands which are either weak or higher member of the sequence. The constants reported by us for the different band systems have been collected in Table 3.

Table 2. Isotopic shift of YCl molecule.

v', v''	$\Delta\upsilon_{ical}$ (cm^{-1})	$\Delta\upsilon_{iobs}$ (cm^{-1})	(v', v'')	$\Delta\upsilon_{ical}$ (cm^{-1})	$\Delta\upsilon_{iobs}$ (cm^{-1})	(v', v'')	$\Delta\upsilon_{ical}$ (cm^{-1})	$\Delta\upsilon_{iobs}$ (cm^{-1})
			C—X System					
1 0	5.7	5.7	4 1	16.6	16.4	5 0	29.9	28.5
2 1	4.6	4.5	5 2	15.3	15.0	7 2	26.9	25.9
3 1	3.4	3.2	6 3	13.9	13.6	8 3	25.3	24.8
2 0	11.9	11.7	7 4	12.7	12.1	9 4	23.8	24.4
3 1	10.6	10.6	4 0	24.0	23.8	6 0	35.7	34.6
4 2	9.4	9.1	5 1	22.5	22.0	7 1	34.1	33.8
5 3	8.1	8.0	6 2	21.1	20.9	8 2	32.5	31.8
6 4	6.9	6.6	7 3	19.7	19.9	9 3	30.9	30.5
3 0	18.0	18.4	8 4	18.3	18.5			
			D—X System					
2 0	12.9	12.4	2 1	5.6	5.3	4 5	-10.0	9.4
3 1	12.0	11.8	3 2	4.8	4.3	0 2	-15.0	14.4
4 2	11.2	11.0	4 3	4.0	3.8	1 3	-15.4	15.0
5 3	10.3	10.4	5 4	3.3	3.1	2 4	-15.9	15.6
6 4	9.5	9.3	0 1	-7.7	-7.5	3 5	-16.4	16.9
7 5	8.6	8.2	1 2	-8.3	-8.0	4 6	-16.8	16.2
8 6	7.8	8.0	2 3	-8.8	-8.2	5 7	-17.7	16.8
1 0	6.3	6.2	3 4	-9.4	-9.1	6 8	-17.7	16.9
			F—X System					
2 0	12.4	11.7	7 5	7.8	7.8	1 3	-15.8	-15.9
3 1	11.4	10.3	4 5	-10.8	-11.4	2 4	-16.4	-17.2
4 2	10.4	9.6	5 6	-11.4	-10.6	4 6	-17.1	-17.9
5 3	9.5	8.5	0 2	-15.1	-15.2	5 7	-17.6	-18.3

$\Delta\upsilon_{ical} = \upsilon_{cal} - \upsilon_{ic}$ $\Delta\upsilon_{in} = \upsilon_{nbs} - \upsilon_{ic}$

Table 3. Summary of the vibrational constants of YCL (in cm^{-1}).

System	υ_{oo}	ω_e	$\omega_e x_e$
F	27102.8	332.1	0.70
E	24322.0	342.5	0.75
D	22773.0	346.0	1.25
C	14879.5	324.5	1.14
X		380.7	1.30

The ground state electronic configurations of yttrium and chlorine atoms are given by :

$$_{39}Y = 1s^2, 2s^2\,2p^6, 3s^2\,3p^6\,3d^{10}, 4s^2\,4p^6\,4d^1, 5s^2 \quad {}^2D$$

$$_{17}Cl = 1s^2, 2s^2\,2p^2, 3s^2\,3p^5$$

Considering the separated atoms model, we have Y with ^2D and Cl with ^2P as their ground states. The combination of these two atomic states gives rise to $\Sigma, \Pi, \Delta, \Phi$ with the

multiplicity of singlet and triplet. In our spectrograms we have identified a few atomic lines of yttrium and all these lines arise from the excited electronic states ^2F, ^2D and ^2P. It is therefore believed that the excited states of YCl responsible for these transitions arise from these excited states of yttrium. The molecular electronic states arising due to the formation of YCl molecule can be derived by the application of separated atoms model considering chlorine atom in its ground state ^2P and yttrium atom in its different excited states. From the literature [7] the resultant molecular electronic states are found as :

Atomic states	Multiplicity	Terms
^2P(Y) + ^2P(Cl)	1 , 3	$\Delta(1), \pi(2), \Sigma(3)$
^2D(Y) + ^2P(Cl)	1 , 3	$\Phi(1), \Delta(2), \pi(3), \Sigma(3)$
^2F(Y) + ^2P(Cl)	1 , 3	$\Gamma(1), \Phi(2), \Delta(3), \pi(3), \Sigma(3)$

Since thermal emission is a low energy process, no intercombination system is expected to appear. Thus only probable transitions are $^1\Sigma$—$^1\Sigma$ and $^1\pi$—$^1\Sigma$ taking $^1\Sigma$ as ground state. Barrow *et al* [8], on the basis of rotational analysis, reported that the ground state for YF molecule is to be $^1\Sigma$. Since YF and YCl molecules are isovalent (*i.e.* belong to same family), we expect YCl to have the same ground state as YF *i.e.* $^1\Sigma$.

In the system C—X and F—X, the observed bands are single headed and well developed, therefore, these systems arise from the transition $^1\Sigma$—$^1\Sigma$. This prediction has been verified by Janney [1] and Simard *et al* [5] for the C—X system by investigating the rotational structure. The two band systems D—X and E—X, lying in the neighbourhood of the line λ 4142.8 Å of yttrium, have the feature of $^1\pi$—$^1\Sigma$ transition.

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